



Plutonium Oxide Gas Generation Testing

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SRTC Gas Generation Testing Objectives

- Measure gas generation rates as a function of:
 - moisture content
 - specific surface area
 - dose rate
 - fill gas composition
- Develop a technical basis to:
 - understand the impact of gas generation on long-term storage of oxides
 - support model development to predict gas generation phenomena (Paffett and Kelly)

Gas Generation Tests

- Tests conducted with ≈ 9 g PuO_2 in SS vessels—free gas volume ≈ 25 mL
- Initial fill gas air, N_2 , Ar, or Ar/ H_2
- Recorded pressure and temperature over time (1 to 3 weeks or longer)
- Sampled headspace gas (not all cases) and analyzed by GC for H_2 and O_2

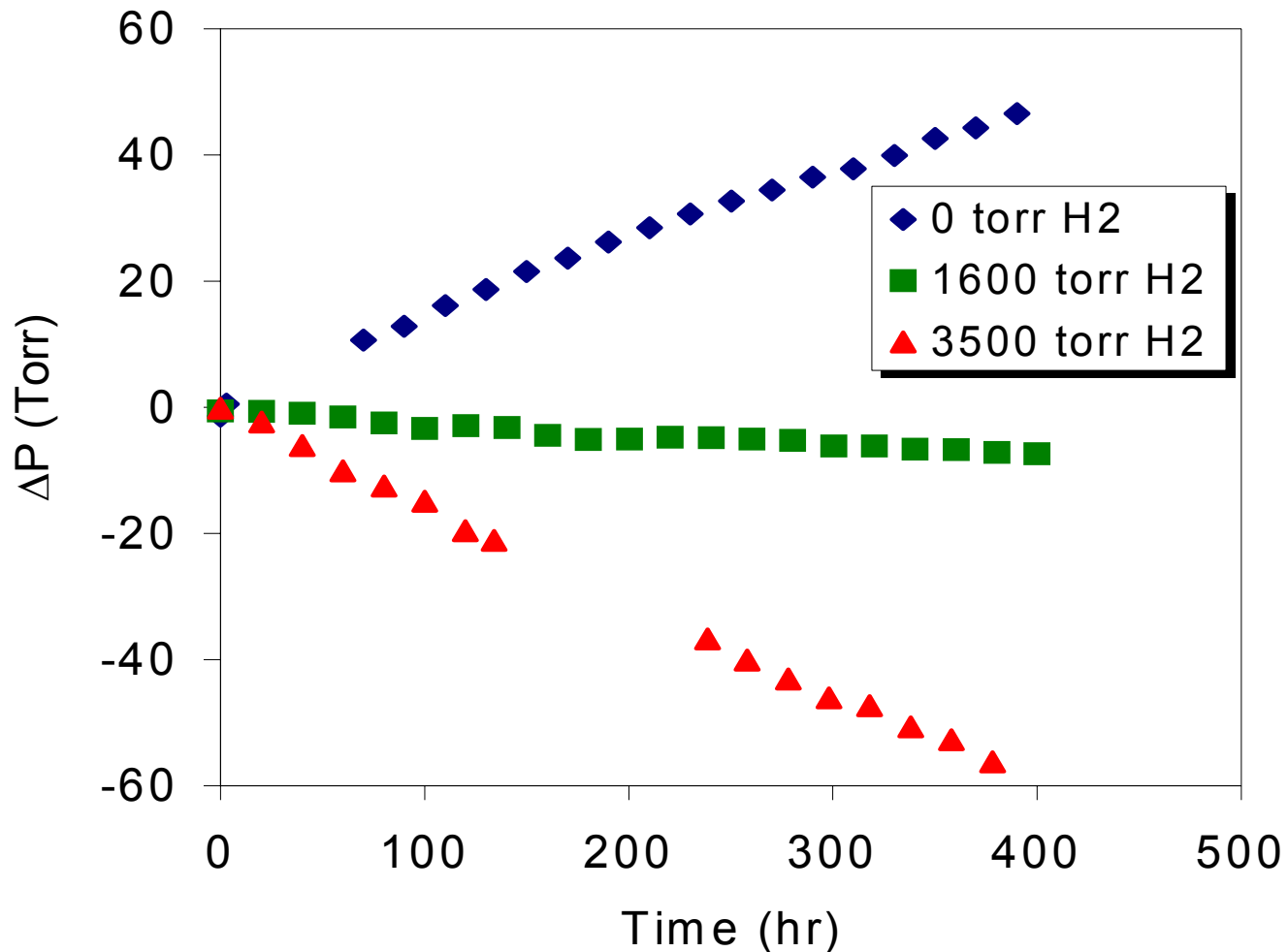




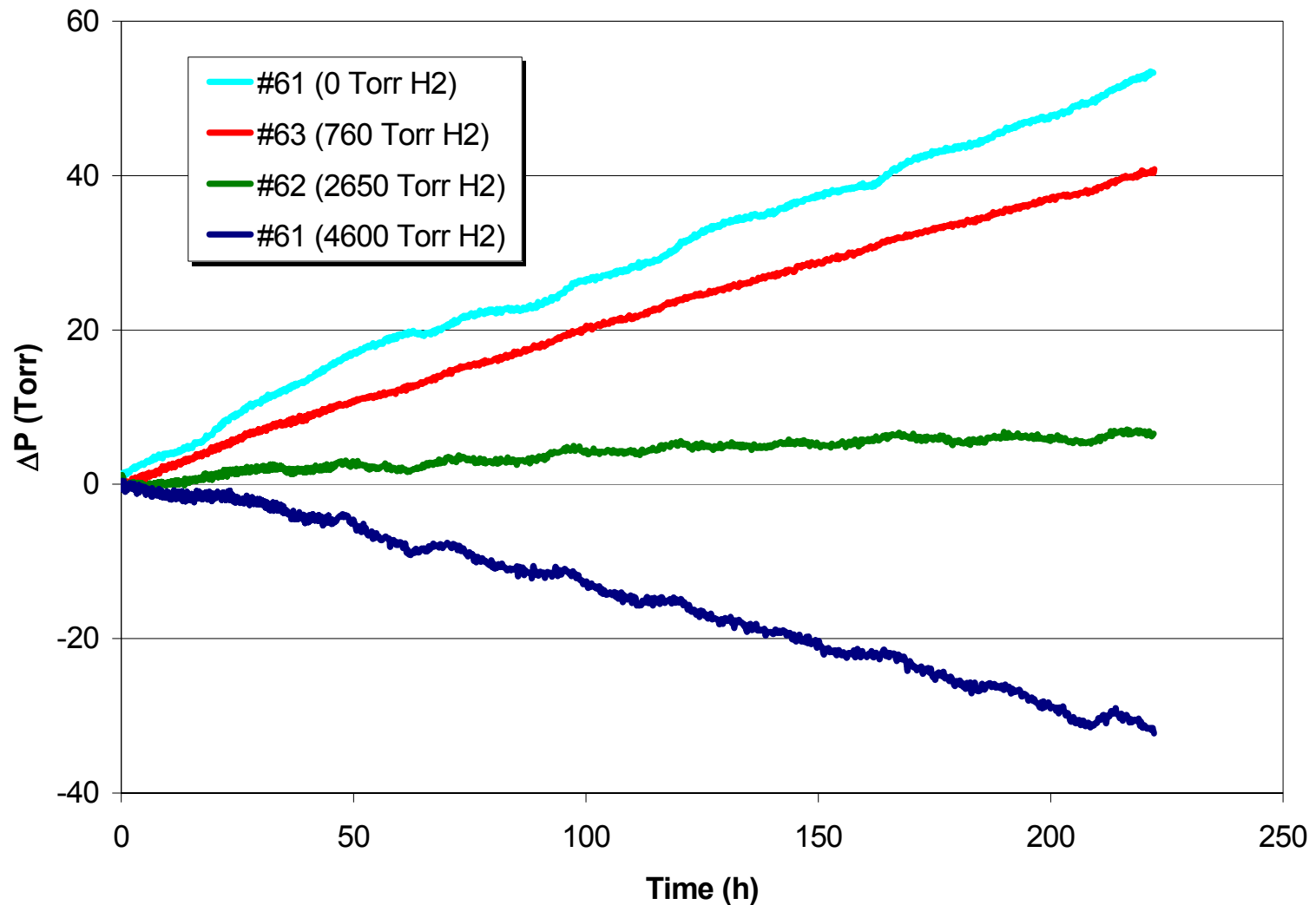
Summary of Work To Date

- Gas generation rates for PuO_2 :
 - increase with moisture content and dose rate
 - decrease with specific surface area
 - impacted by headspace gas composition
- H_2 generation rates slow at moisture contents < 0.5 wt %; O_2 is consumed
- Rate of container pressurization decreases with H_2 pressure (and Ar pressure)
- Apparent steady state reached at pressures much lower than supported by STD-3013 container design

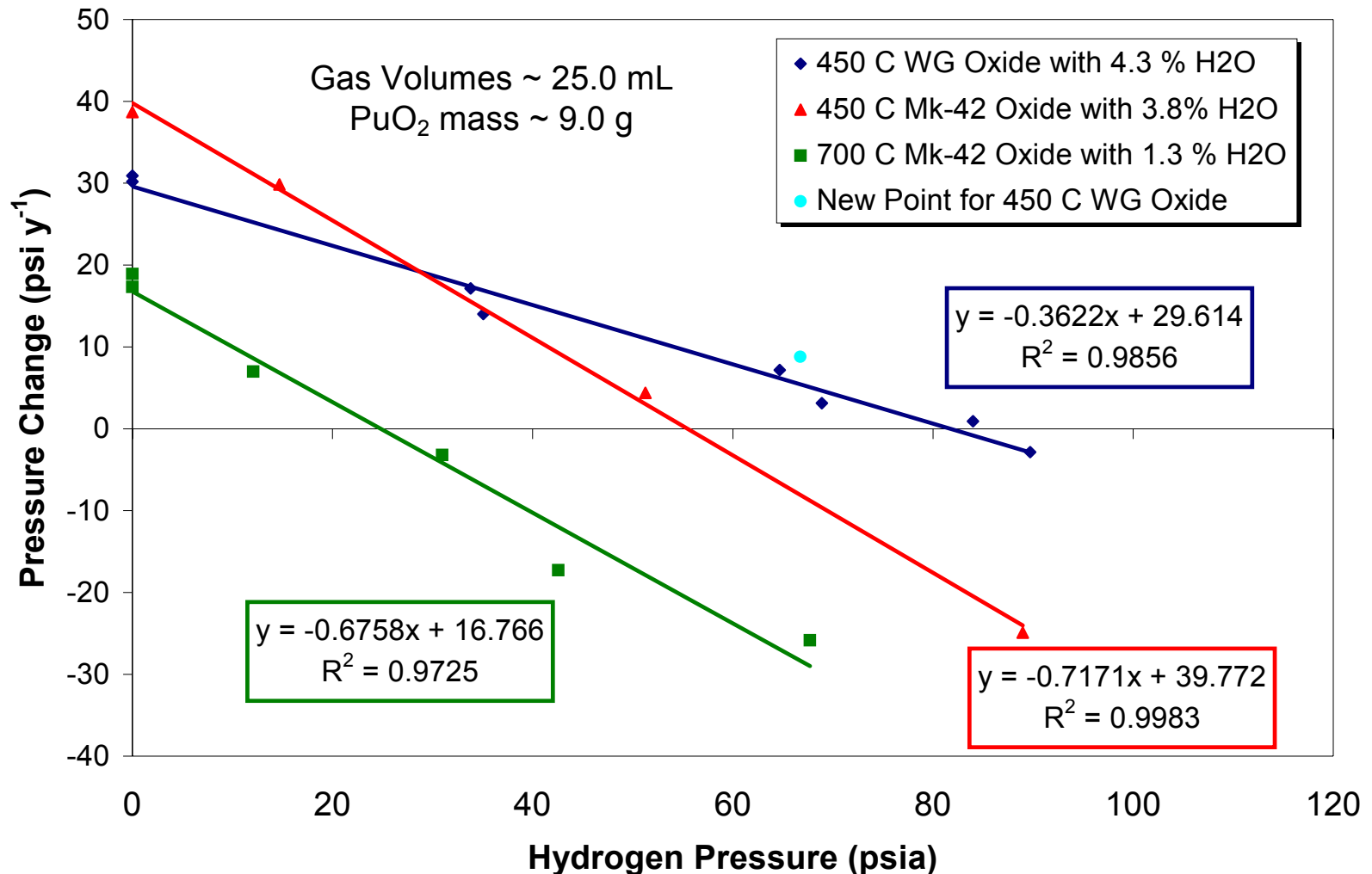
Effect of Initial H₂ Pressure on 700 °C Mark 42 Oxides with 1.3% H₂O



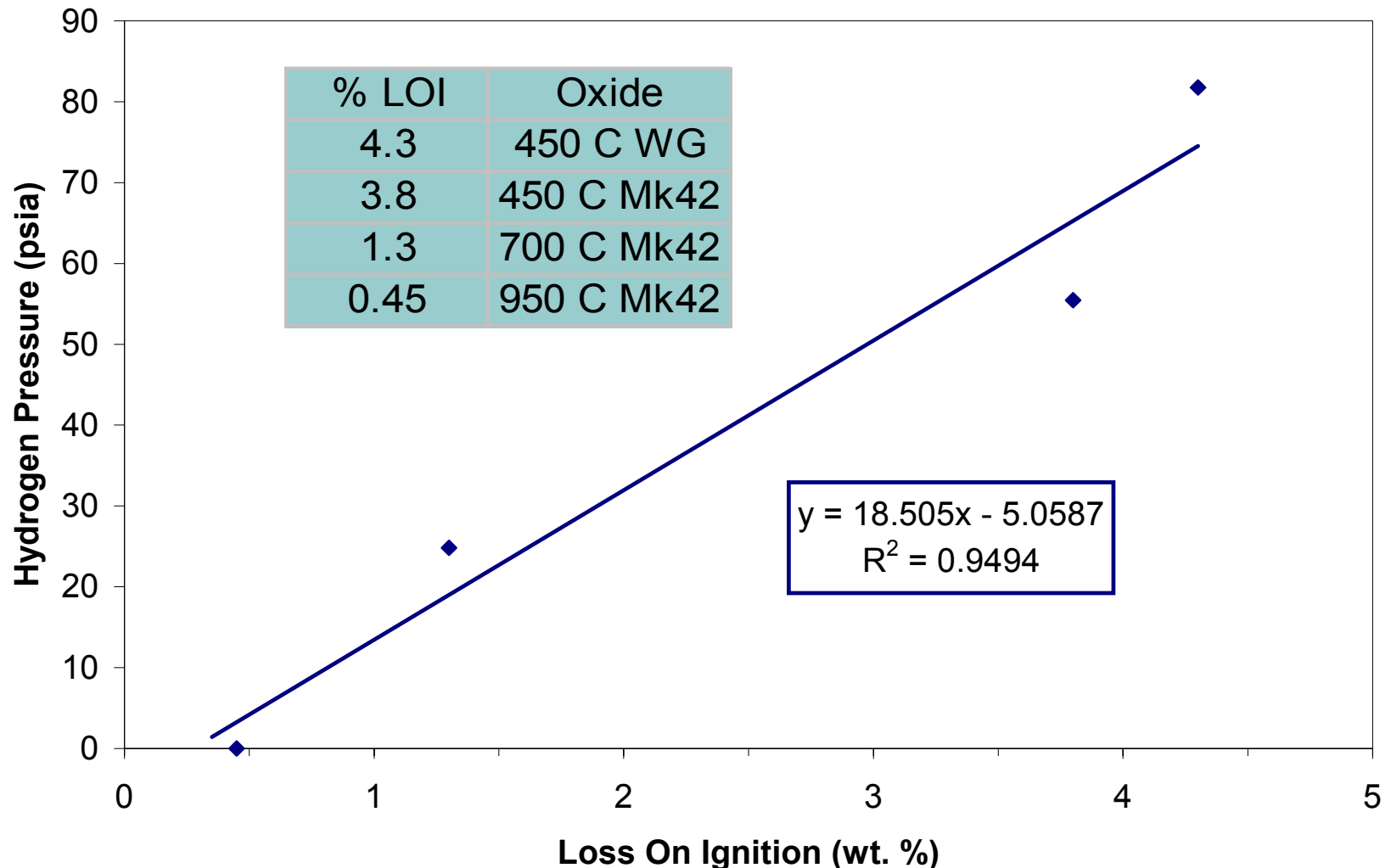
Effect of Initial H₂ Pressure on 450 °C Mark 42 Oxides with 3.8% H₂O



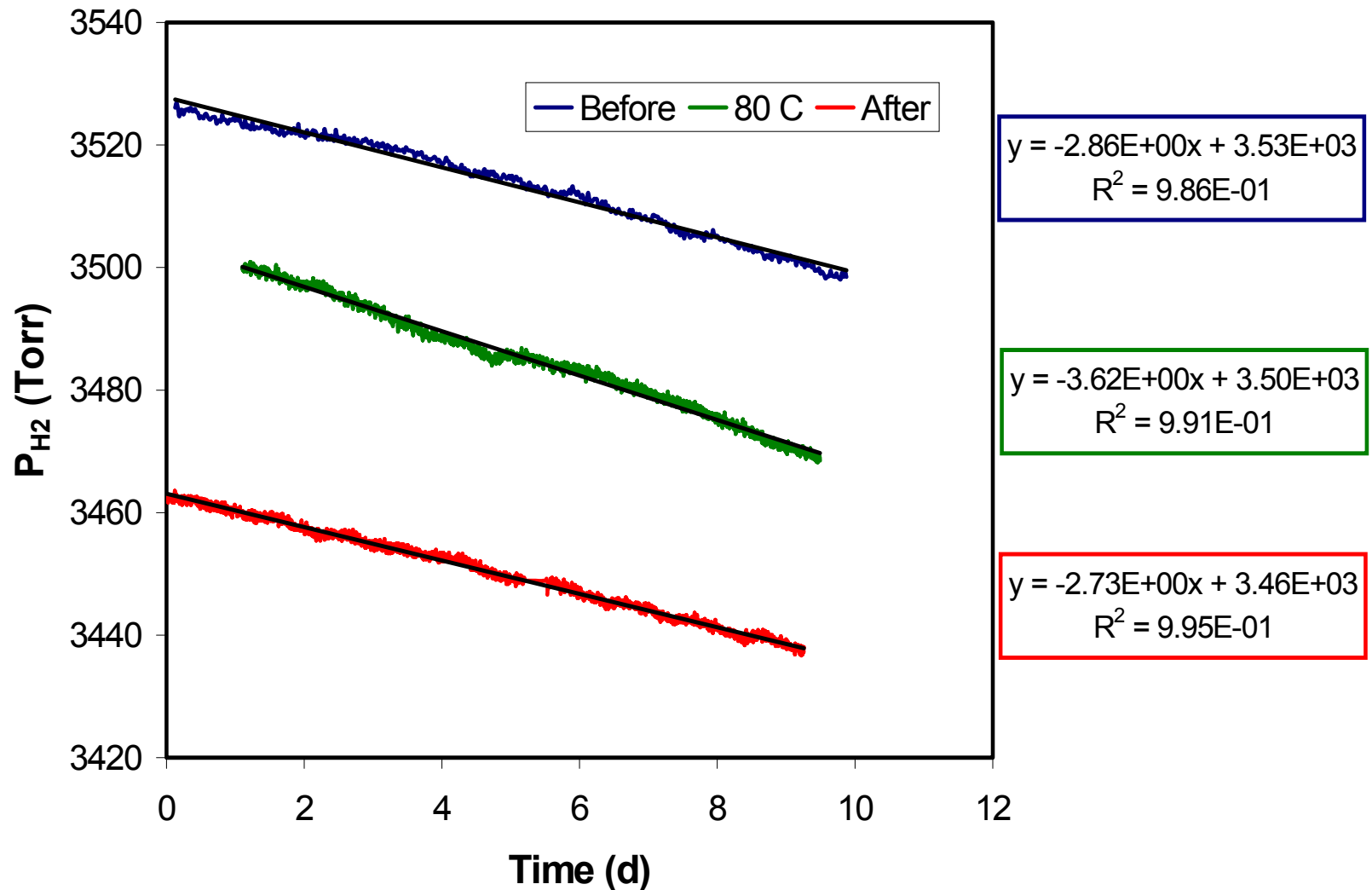
Rate of Container Pressurization Decreases Linearly with H₂ Pressure



Apparent Steady-State H₂ Pressure vs. Loss on Ignition



Effect of Heating on Rate of H₂ Removal for Mark 42 950 °C Oxide with 0.4% H₂O





Outline

- Background and Test Objectives
- Test Equipment and Design
- Test Conditions and Results
- Limitations of Existing Data
- Test Equipment Upgrades
- Proposed Tests for FY'03
- Discussion of Related Activities



Limitations of Current Tests

- Moisture measurement accuracy
- Single gas composition measurement
- Volume require for gas analysis
- Sensitivity of rate measurement limited by void volume
- Specific surface areas are estimated - not measured



Related Activities

- NpO_2 Gas Generation Testing
- Transportation of NpO_2
- Installation of new SEM and XRD



Test Equipment Upgrades

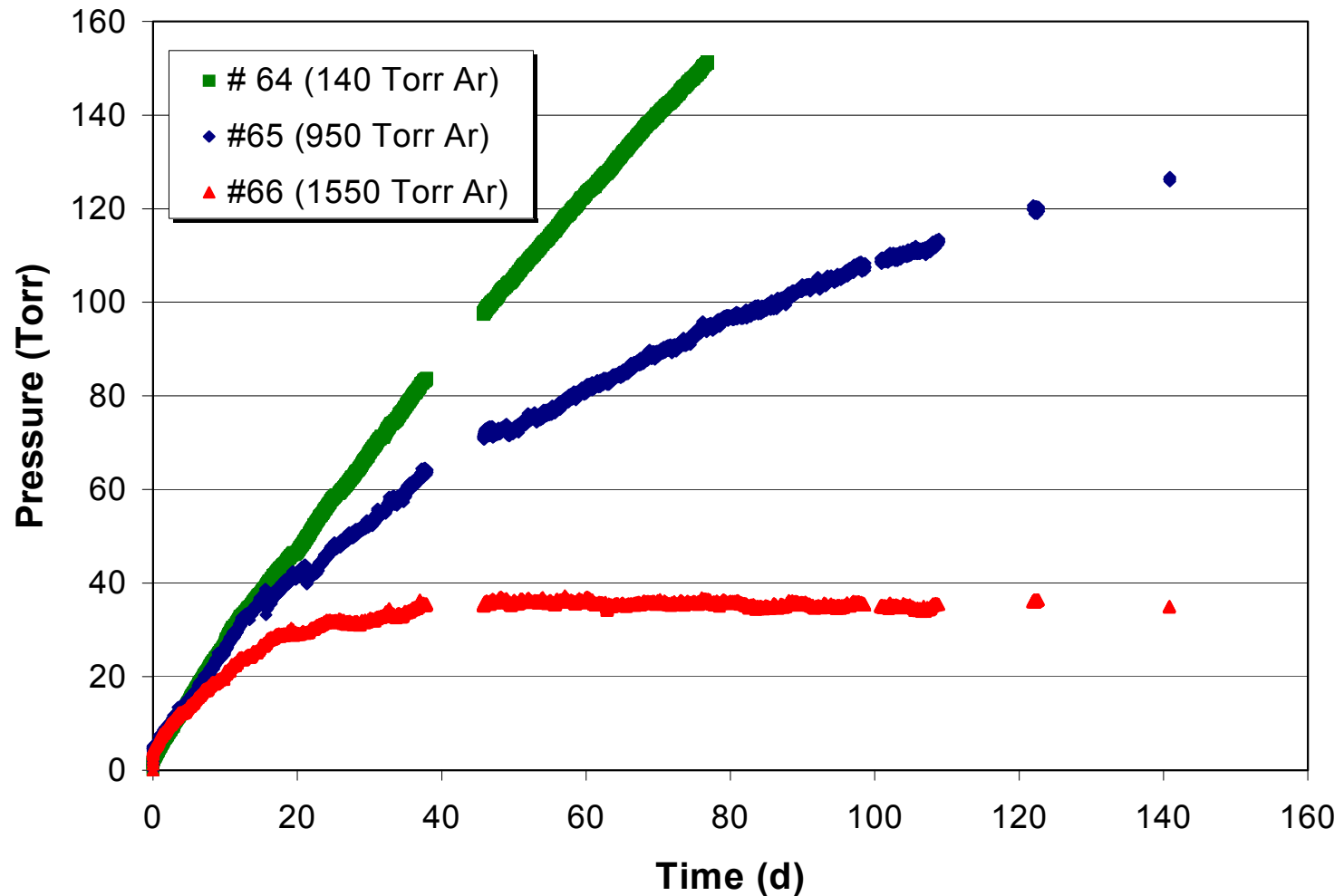
- Replace test vessels
 - integrated pressure transducer
 - sample volume <1% of void volume
 - inserts for small samples
- Include corrosion test specimens
- TGA-MS for moisture analysis
- BET for specific surface area

Proposed Tests for FY'03

H₂ generation rate as a function of:

- Water form (hydroxide, hydrate, hydroxyl and free water)
- Temperature
- Salts(CaCl₂, MgCl₂)
- Energy Transfer (Ga₂O₃, ZrO₂)
- Oxyanions (SO₄, NO₃, CO₃)
- Other (carbon, teflon)

Effect of Argon Pressure on Rate of Container Pressurization





Future Work

- Further evaluate the mechanism for reaching apparent steady state pressure at elevated H₂ and Ar pressures
- Measure effect of impurities on gas generation rates
- Investigate the impact of temperature on gas generation rates
- Measure oxide surface areas and improve moisture measurement capabilities

Micro GC Installation in SRTC

